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THE STRUCTURE OF METAL KETYLs DERIVED FROM
XANTHONE ANALOGUES IOn the Electronic Structure of Monomer Metal Ketyl_s

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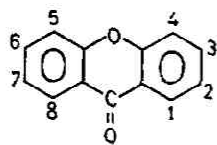
IWA0 TANIMOTO AND JIRO OSUGI

The structure of metal ketyl_s derived from xanthone, thioxanthone and selenoxanthone was studied. It was found that in solution there are two types of paramagnetic species in these ketyl_s by the method of ESR technique. One is the monomer type and the other is dimer type. In this paper the electronic distribution on monomer ketyl_s of xanthone analogues was examined. The correlation between structure and spin density was also discussed.

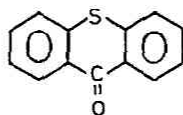
Introduction

Metal ketyl_s were originally discovered by Beckman and Paul¹⁾ in 1891 and recognized as free radical by Schlenk and Weichel²⁾ in 1911. Since the ESR technique began to be applied to the field of the organic free radical chemistry, metal ketyl_s have been investigated extensively by the method for the last 15 years³⁾. These investigations have revealed the electronic, structural and kinetic aspects of metal ketyl_s in solutions and in rigid media.

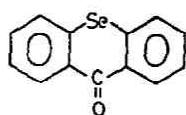
In this paper the electronic distribution on monomer metal ketyl_s of xanthone analogues [I], [II], [III] which were produced by the reduction of the corresponding ketones with alkali or alkali earth metals will be reported. The metal ketyl_s examined here were stable in the absence of air and moisture.



[I]



[II]



[III]

(Received June 22, 1969)

1) F. Beckman and T. Paul, *Ann.*, **266**, 1 (1891)2) W. Schlenk and T. Weichel, *Ber.*, **44**, 1182 (1911)3) For example, N. Hirota "Metal Ketyl_s and Related Radical Ions", in "Radical Ions", ed. by E. T. Kaiser and L. Kevan, Interscience Publishers (1968)

Experimental

Materials

Xanthone obtained from Nakarai Chemical Co. Ltd. was recrystallized from benzene-ethanol, white needle, mp 174°C. Thioxanthone was prepared from thiosalicilic acid and benzene treated with concentrated sulfuric acid according to Davis and Smiles' method⁴⁾. It was recrystallized from ethanol, yellow needle, mp 209°C. Selenoxanthone was prepared from selenosalicilic acid and benzene treated with anhydrous aluminium chloride according to Lesser and Weiss' method⁵⁾. It was recrystallized from ethanol, yellow needle, mp 192°C.

Preparation of metal ketyls

Various ketyls were prepared by the reduction of ketones with alkali and alkali earth metals. Metallic sodium and potassium were purified by distillation in vacuum and contacted with ketone dissolved in tetrahydrofuran. Metallic lithium, calcium and barium can't be distilled in a glass tube and so they were reacted in the state of mercury amalgam. All reactions were carried out in a sealed off glass apparatus equipped with a cell for the ESR measurement.

The coupling constant due to nitrogen atom of Fremy's salt was used as a standard.

Results and Discussion

The preparation and the ESR measurements of metal ketyls were carried out by the usual methods described previously⁶⁾. By the preliminary experiments, it was found that two different kinds of paramagnetic species could be present in the solution for each of metal ketyls derived from [I], [II] and [III]. Furthermore, each of the two paramagnetic species could be observed separately as the main component by the ESR spectroscopy if the optimum experimental condition was suitably selected. The two paramagnetic species may correspond to monomer metal ketyl and to dimer metal ketyl.*⁷⁾ Here, we shall deal with the monomer metal ketyls of [I]~[III]. Here, especially, on the aspect of the molecular structure, of the ion pair formation and of the distribution of unpaired electron. Although our wishes to make Te analogue of xanthone remain unsuccessful yet, the metal ketyls examined are of interest in the point of their electronic distribution, for [I], [II] and [III] have a bridge connecting two phenyl groups of benzophenone in their structural aspect, that is a bridge constructed from the atoms belonging to group VIa in the periodic table. Metal ketyls of [I] and [II] have been investigated separately by two research groups⁷⁾⁸⁾, but we have reinvestigated them in detail.

Xanthone Ketyls

As soon as xanthone dissolved in tetrahydrofuran is contacted with metals, it reacts and blue

4) E. G. Davis and S. Smiles, *J. Chem. Soc.*, **97**, 1296 (1910)

5) R. Lesser and R. Weiss, *Ber.*, **57**, 1078 (1924)

6) K. Maruyama, R. Tanikaga and R. Goto, *Bull. Chem. Soc. Japan*, **36**, 1141 (1963)

7) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964)

8) E. T. Kaiser and D. H. Eagle, *ibid.*, **85**, 1821 (1963)

*) For the dimer we shall report in the succeeding paper.

color appears. The ketyls are very stable, but they gradually decompose with heat and light. Each of the spectra of ketyls derived by the reduction of xanthone with several kinds of alkali and alkali earth metals consists of five major groups of lines *i.e.* intensity ratio; 1 : 4 : 6 : 4 : 1, the total width is between 17~19 gauss. Each group splits three groups of lines *i.e.* intensity ratio; 1 : 2 : 1. Therefore, analyses of spectra were quite straightforward. The coupling constants due to metals were usually very small (see Fig. 1 and Table 1).



Fig. 1 ESR spectra of xanthone ketyls

- (a) potassium ketyl
(b) calcium ketyl

The spectrum of lithium ketyl showed the alternating line broadening at room temperature (Fig. 2), but this disappears below -20°C . The phenomenon of the line broadening has already been reported as the problem of rotation isomer in radical anions of nitrobenzaldehyde⁹⁾ and dinitro-durene and as the problem of position isomer of counter ion in the radical anion of piracene¹⁰⁾. The

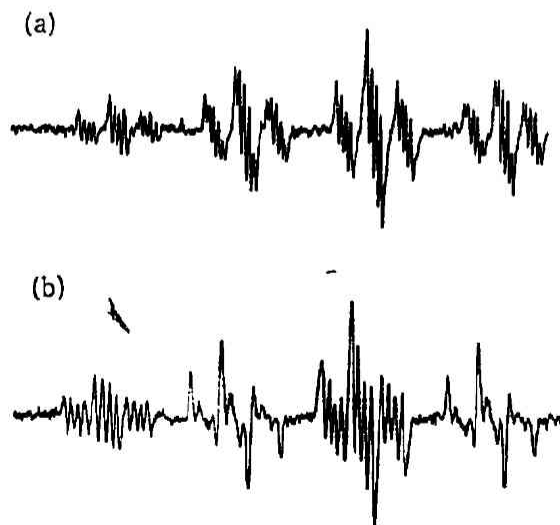


Fig. 2 ESR spectra, lithium ketyl of xanthone

- (a) at -20°C
(b) at room temperature

9) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1951); J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 699 (1964)

10) E. de Boer and E. L. Makor, *Proc. Chem. Soc.*, **23**, (1963)

alternating line broadening observed in the lithium ketyl may be ascribed to the position isomer of lithium cation between carbonyl oxygen and bridging oxygen atom with which two phenyl groups of benzophenone are linked.

Thioxanthone Ketyls

Thioxanthone was more reactive than xanthone with metals. Kaiser and Eagle have investigated solely on the potassium ketyl of thioxanthone⁶⁾ and reported that its spectrum consisted of five major lines with coupling constant of 3.5 gauss due to four equivalent protons. The spectra observed in this study consist of lines due to four pairs of equivalent protons; 1,8-, 3,6-, 4,5- and 2,7-protons. The assignment is different from Kaiser's, but ours is more reasonable by referring to the spectra of calcium and barium ketyls of thioxanthone (Fig. 3 and Table 1).

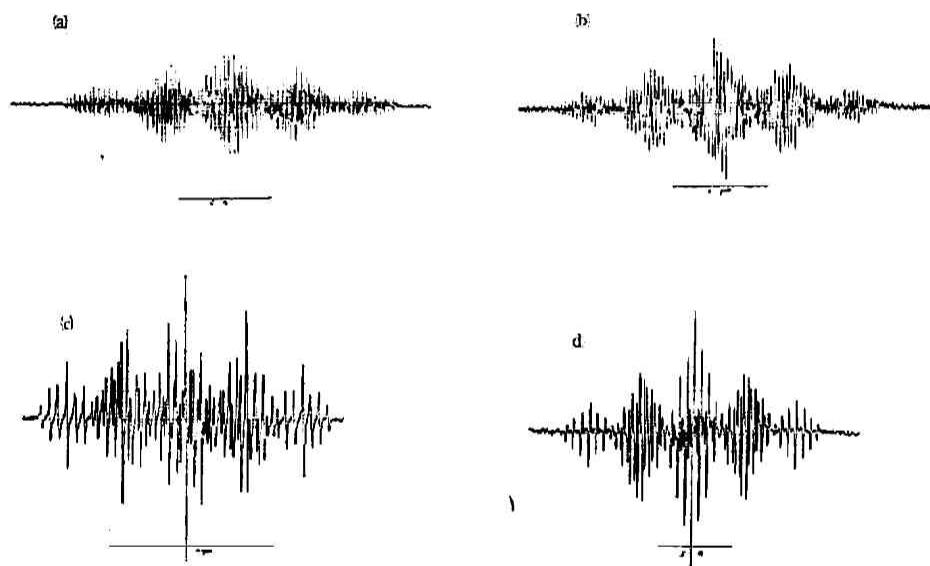


Fig. 3 ESR spectra of thioxanthone ketyls

- | | |
|-------------------|---------------------|
| (a) lithium ketyl | (b) potassium ketyl |
| (c) calcium ketyl | (d) barium ketyl |

Selenoxanthone Ketyls

The behavior of selenoxanthone ketyls was quite similar to that of thioxanthone ketyls. The spectra consist of five major groups of lines due to four pairs of two equivalent protons (Fig. 4 and Table 1).

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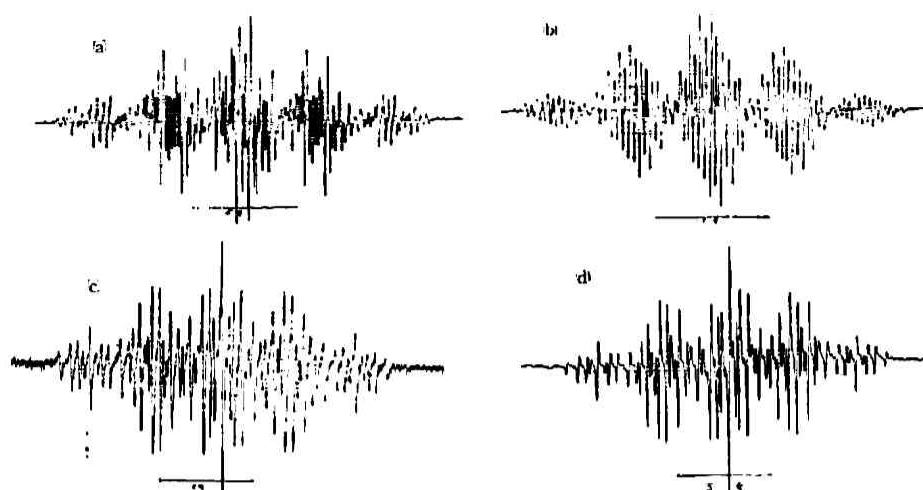
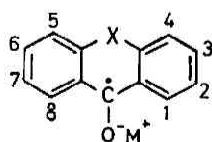


Fig. 4 ESR spectra of selenoxanthone ketyls
(a) lithium ketyl (b) potassium ketyl (c) calcium ketyl (d) barium ketyl

Table 1 Coupling constants analyzed from spectra of xanthone-, thioxanthone- and selenoxanthone-ketyl at the room temperature, in tetrahydrofuran

Metal	X	Coupling constant					T.W.	S.D.
		proton				metal		
		1,8	2,7	3,6	4,5			
Ca	O	3.88	0.17	3.88	0.96	—	18.15	—
	S	3.42	0.53	3.84	1.05	—	18.08	—
	Se	3.30	0.66	3.69	1.16	—	17.75	—
Ba	O	3.72	0.14	3.72	0.93	—	18.65	—
	S	3.36	0.52	3.70	1.03	—	18.00	—
	Se	3.27	0.64	3.65	1.05	—	17.75	—
Li	O	3.86	0.06	3.86	0.96	0.19	18.50	0.0013
	S	3.39	0.11	3.80	1.07	0.27	18.20	0.0019
	Se	3.24	1.15	3.70	1.35	0.34	18.05	0.0024
Na	O	3.72	0.10	3.72	1.00	0.20	18.50	0.00063
	S	3.41	0.11	3.72	0.99	0.22	17.65	0.00069
	Se	3.31	—	3.70	1.00	0.24	17.25	0.00076
K	O	3.88	0.10	3.88	0.91	0.19	17.92	0.0023
	S	3.44	0.15	3.71	1.02	0.21	17.57	0.0025
	Se	3.32	—	3.70	0.96	0.24	17.28	0.0029



X: O, S, Se

T.W.: total width of spectrum

S. D.: spin density on metal

Q-values*) of metals were used the

followings; Li: 143.5 G, Na:

316 G, K: 82 G

*) B. J. Herald, A. F. Neiva Correia and J. dos Santos Veiga, *J. Am. Chem. Soc.*, **87**, 2661 (1965)

As it is reasonable to consider the following valence bond structures for the ketyls of xanthone analogues, the assignments of the coupling constants to the corresponding protons were done tentatively in reference to the result of HMO calculation (Fig. 5).

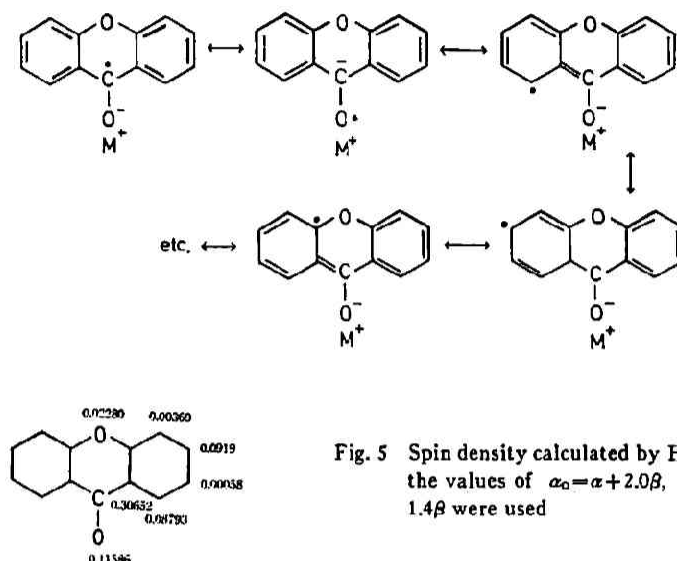


Fig. 5 Spin density calculated by HMO; the values of $\alpha_0 = \alpha + 2.0\beta$, $\beta_{\text{CO}} = 1.4\beta$ were used

Examination of the observed ESR spectra elucidates the following tendencies.

- i) Estimating from the spin density on metals, the covalency of the bond between carbonyl oxygen and metal increases in the order of xanthone-, thioxanthone- and selenoxanthone-ketyl.
- ii) The total width of the spectrum decreases in the same order to that of i).
- iii) Although the coupling constants due to $H_{1,8}$ -protons and $H_{3,6}$ -protons decrease, in general, in the order of xanthone-, thioxanthone- and selenoxanthone-ketyl, there are sharp differences among the coupling constants due to $H_{1,8}$ -protons and $H_{3,6}$ -protons for the latter two ketyls, whereas the coupling constants due to the corresponding two pairs of protons are quite the same for the xanthone ketyl.

The tendencies i) and ii) indicate that the delocalization of unpaired electron on the whole molecule decreases in the order of xanthone-, thioxanthone- and selenoxanthone-ketyl. This may be ascribed to the loss of the coplanarity of two phenyl groups in the same order as in the increase of the covalent radii of bridging atoms (O : 0.66\AA , S : 1.04\AA , Se : 1.16\AA). However, it is hard to give a simple explanation for the tendency iii). Probably such a tendency must result from the complex combination of atomic size and electronic nature of the bridging atoms.

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